Adsorption behaviour of cationic fixatives and their effect on pitch deposition

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SUMMARY

The behaviour of the four different polymeric fixatives in the presence of wood extractive components with and without fibres was investigated. Cationic polyacrylamide (CPAM) and high and medium charge co-polymers of polyacrylamide and poly(diallyl-dimethyl ammonium chloride (polyDADMAC) were found to stabilise the wood extractive colloids in solution, as well as to attach the wood resins to the fibre. Polyethylenimine (PEI) was shown to cause non-selective deposition onto both fibre and non-fibre surfaces, as well as reduce the amount of wood extractives in the dissolved and colloidal phase. PEI was also found to preferentially interact with triolein and the medium charge co-polymer exhibited preference in fibre-attachment of oleic acid.

INTRODUCTION

During the production of thermo-mechanical pulp, resinous wood components are released into the process waters. This material can form pitch deposits and interfere with paper production. Additionally, discharge of large amounts of this resinous material in the effluent poses an environmental problem due to their natural toxicity. The accumulation of the resinous material in the process water can also prevent further closure of the system and reduction of water usage.

Cationic polymers are added to fibre suspensions in an attempt to prevent the agglomeration of the wood resins and thereby control pitch deposition. These cationic polymers are considered to cause adsorption of the wood resins onto fibres and they are commonly termed fixatives. Many pitch fixatives are available. Norske Skog have conducted several studies to determine the best fixative in different situations (*3-6*). There is little genuine understanding, however, of why different fixatives appear to work for different systems (*7-10*) as there are no discernible trends in the data and little is known about the fixatives themselves.

Extensive work has been undertaken by our research group to understand the interactions between the major wood extractive components and their effect on deposition (*1,11*). This paper describes work which extends the previous studies by investigating deposition behaviour when cationic polymeric fixatives and fibres are added to model pitch dispersions. The interaction of four fixatives (polyethylenimine (PEI), cationic polyacrylamide (CPAM) and two co-polymers of polyacrylamide and poly(diallyl-dimethyl ammonium chloride (polyDADMAC) of differing charge demand) with three model pitch extractives (abietic acid, oleic acid and triolein) was studied both with and without fibres. The major aim of this study is to investigate the interaction between different fixatives and different components of the wood extractives, as well as fibres, in order to gain a better understanding the interactions that occur in the white-water system.

EXPERIMENTAL

Model pitch dispersions were made from a fatty acid (oleic acid, Aldrich 99+% purity [112-80-1]), a triglyceride (triolein, Sigma 99 % purity [122-32-7]) and a resin acid (abietic acid, Aldrich 70 % purity technical grade [514-10-3]) using dialysis techniques previously described (*12*). For the experiments the concentrations of wood extractive components were 60mg/L abietic acid, 10mg/L oleic acid and 45mg/L triolein.

Extractive-free fibres were prepared by Soxhlet extraction with hexane of TMP pulp made from *Pinus radiata*. The extractive-free air-dried fibres were made down to a 3% stock consistency with distilled water and homogenised through low shear agitation. Unused dry fibres were stored in the freezer.

Deposition was conducted by stirring 400mL of the dialysed model pitch dispersions in polyethylene (PE) jars using a paddle stirrer (Cole Palmer, PE coated). Stirring occurred for a period of two hours for those experiments without fibres and 30 minutes for those with fibres at 50°C. A constant stirring rate of 330 rpm was used. All deposition measurements were conducted at pH 7.0.

The model pitch components were extracted from the dispersions, before and after deposition, using tertiary butyl methyl ether (t-BME). They were then silylated and analysed by gas chromatography (GC) analysis as described previously (*13*).

The quantity of the individual components deposited onto non-fibre surfaces was determined by the difference between the pre and post deposition concentrations (*14*). For experiments involving fibres, 5 mL aliquots of the dissolved and colloidal substances (DCS) and the fibres/DCS total mixture were taken. The dissolved and colloidal fraction was obtained by centrifuging a sample of the total solution for 10 minutes at 1800 rpm or until the fibres settled. Both samples were extracted using *t*-BME. The amount of fibre bound extractives was determined from the difference between the total fibre/DCS and the DCS amounts.

The charge density of each polymer at 10mg/L (based on dry ingredient) was determined by titration with 0.001N polyethene sodium sulphonate (PES-Na) using a Mütek™ PCD-02 (Particle Charge Detector) to determine charge neutralisation. The charge demand on the extracted fibres was determined by adding excess poly-DADMAC and back titrating with 0.001N PES-Na using a Mütek™ PCD-02 to determine charge neutralisation. The cationic charge demand of the extracted fibres was found to be 8.6μeq/g of pulp.

RESULTS AND DISCUSSION

The charge density of each of the four polymers was measured at pH 6, 7 and 8. The results, which are presented in Table

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Table 1
Polymer Charge Density and Charge Demand

Fixative	Supplier's Rating	pH	Charge Density (μeq/g)	Charge demand (μeq/L)
PEI	Medium	6	4.14	4250
		7	2.00	2050
		8	0.97	958
CPAM	Medium	6	1.87	2170
		7	1.04	1210
		8	1.00	1160
Copoly A	Medium	6	3.48	3280
		7	3.41	3230
		8	3.39	3220
Copoly B	High	6	5.33	5860
		7	5.39	5550
		8	5.33	5580

1, indicate that the charge of the PEI and CPAM is affected by pH while the two co-polymers are not and that even though three of the fixatives are classified as medium charge density they do have slightly different charge densities.

Deposition in absence of fibres

The effect of the different fixatives on the deposition tendency of each of the three wood extractive components of abietic acid, oleic acid and triolein was investigated in both single and three component systems in the absence of fibres. The fixative addition was 10mg/L and this is equivalent to 1kg/tonne added in the presence of fibres. The results are presented in Figure 1. The three component system is when the fatty acid, resin acid and triglyceride are all present and the single is when only one extractive component is included.

Deposition behaviour of the three model components is known to be influenced by the composition of the model pitch dispersions (*15*). The results presented in Figure 1 show that abietic acid and oleic acid have a strong tendency to deposit both as single components and when part of a three component system, at pH 7. The deposition behaviour of triolein is significantly affected by whether it is a single component or part of a three component dispersion. As a single component it has a strong tendency to deposit but when present as part of the three component system its deposition tendency is reduced.

The results suggest a stabilising interaction between the three components is occurring, reducing triolein deposition. Previous work supports this proposed interaction (*1*), as triolein is thought to be encapsulated in a band of oleic and abietic acid molecules when the three components are present. In order to explain the difference in behaviour between the components it is believed that only a small amount of abietic and oleic acid is needed to stabilise the triolein as a colloidal particle and most of the abietic acid and oleic acid interact with each other to form a more hydrophobic particle that deposits readily.

McLean (*11*) has suggested that a critical molar ratio of abietic acid: oleic acid: triolein exists for stabilisation. This molar ratio (1:4:11) was based on a mass ratio of 1:3.7:32.2. In order to stabilise the 45mg/L triolein in solution only 1.4mg/L abietic acid and 4.2 mg/L oleic acid is needed. This is only approximately 2% of the abietic acid present and approximately 40% of the oleic acid. The results suggest that there is even less oleic acid than this 40% interacting in the stabilised complex as 90% of the oleic acid appears to deposit in the three component system. It is not clear at this stage whether several

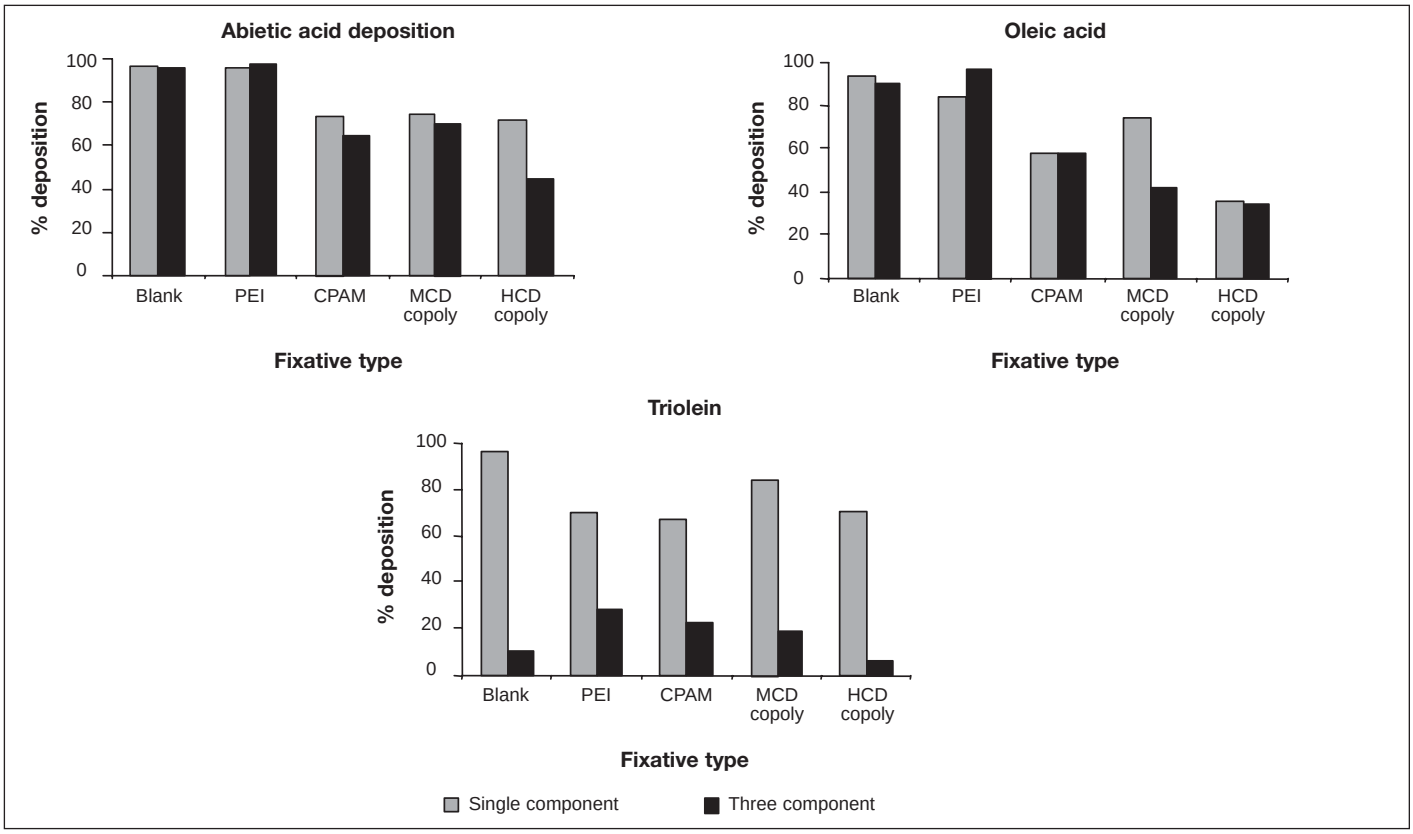

Fig. 1 The effect of fixatives on the deposition behaviour of wood resin extractives in the absence of fibres at pH 7.

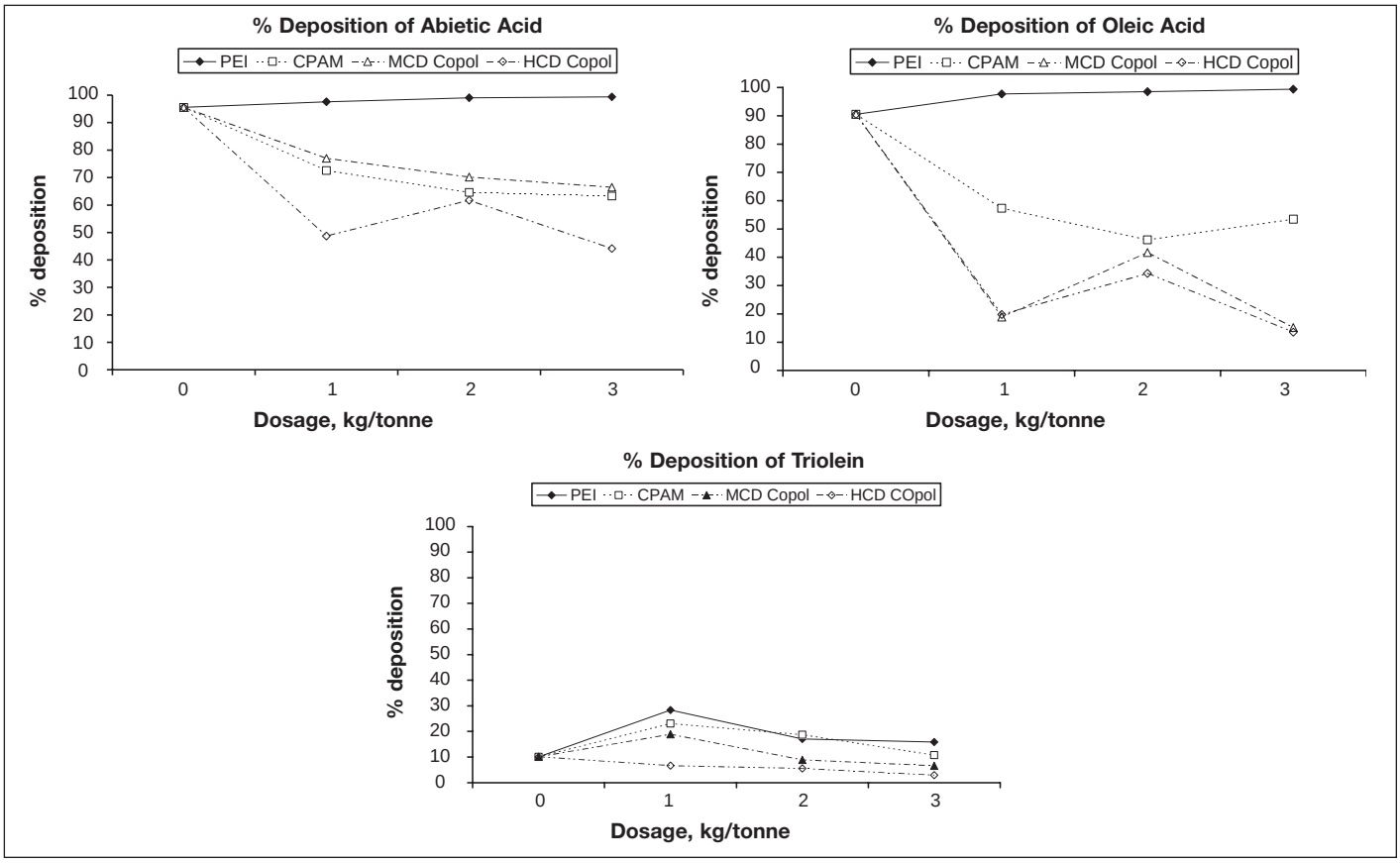

Fig. 2 Deposition behaviour of abietic acid, oleic acid and triolein based on fixative dosage

different types of colloidal particles are present (i.e. a three component encapsulated particle, a more hydrophobic two component particle and also individual resin acid particles) or whether a layered particle is formed in which the outer layer is readily removed and deposited.

Addition of the fixatives to the model pitch dispersions was found to affect deposition tendency of the three components in slightly different ways. CPAM and the two co-polymers were found to decrease the deposition tendency of oleic acid and abietic acid. The high charge density (HCD) co-polymer appears to decrease abietic acid deposition more in the three component system than in the single component system. The medium charge density (MCD) co-polymer was found to have a similar effect on oleic acid. PEI was found to have little apparent effect on the deposition tendency of oleic and abietic acid.

All the fixatives appear to reduce the deposition tendency of triolein when it is a single component with PEI, CPAM and the HCD co-polymer being slightly better than the MCD co-polymer. The deposition of the triglyceride in the three component dispersion is low across all the fixatives types. A slight increase in triolein deposition was observed to occur with the addition of PEI, CPAM and the MCD co-polymer. This indicates that the fixatives reduce the stability of the three component complex but stabilise the individual and two component particles in the colloidal dispersion.

Figure 2 shows the effect of fixative dosage on the deposition behaviour at 10, 20 and 30 mg/L of the four fixatives in a three component system at pH 7. These concentrations correspond to 1, 2 and 3 kg/tonne in the presence of fibres. The optimal dosage when fibres are absent appears to be 15 mg/L for reducing deposition for abietic and oleic acid and 10mg/L for triolein. The decrease in deposition tendency for CPAM and the co-polymers indicates they may be interacting with the components and stabilising them in solution. PEI did not alter deposition tendency compared to the blank, particularly for abietic and oleic acid. This suggests that PEI is either not interacting with the extractives or is interacting and causing surface deposition.

Deposition in presence of fibres

The effect the various fixatives (at 1kg/tonne addition and pH 7) had on the amount of total wood resin bound to fibres, in dissolved / colloidal form (DCS) and bound to non-fibre surfaces when abietic acid, oleic acid and triolein were mixed in a three component system is shown in Figure 3. The three component

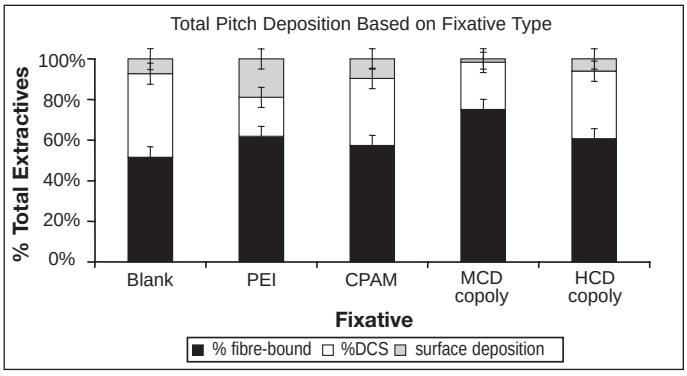

Fig. 3 Effect of different fixatives on total extractive deposition in the three-component system (Error Bars indicate +/- 1 Std. Dev. from mean)

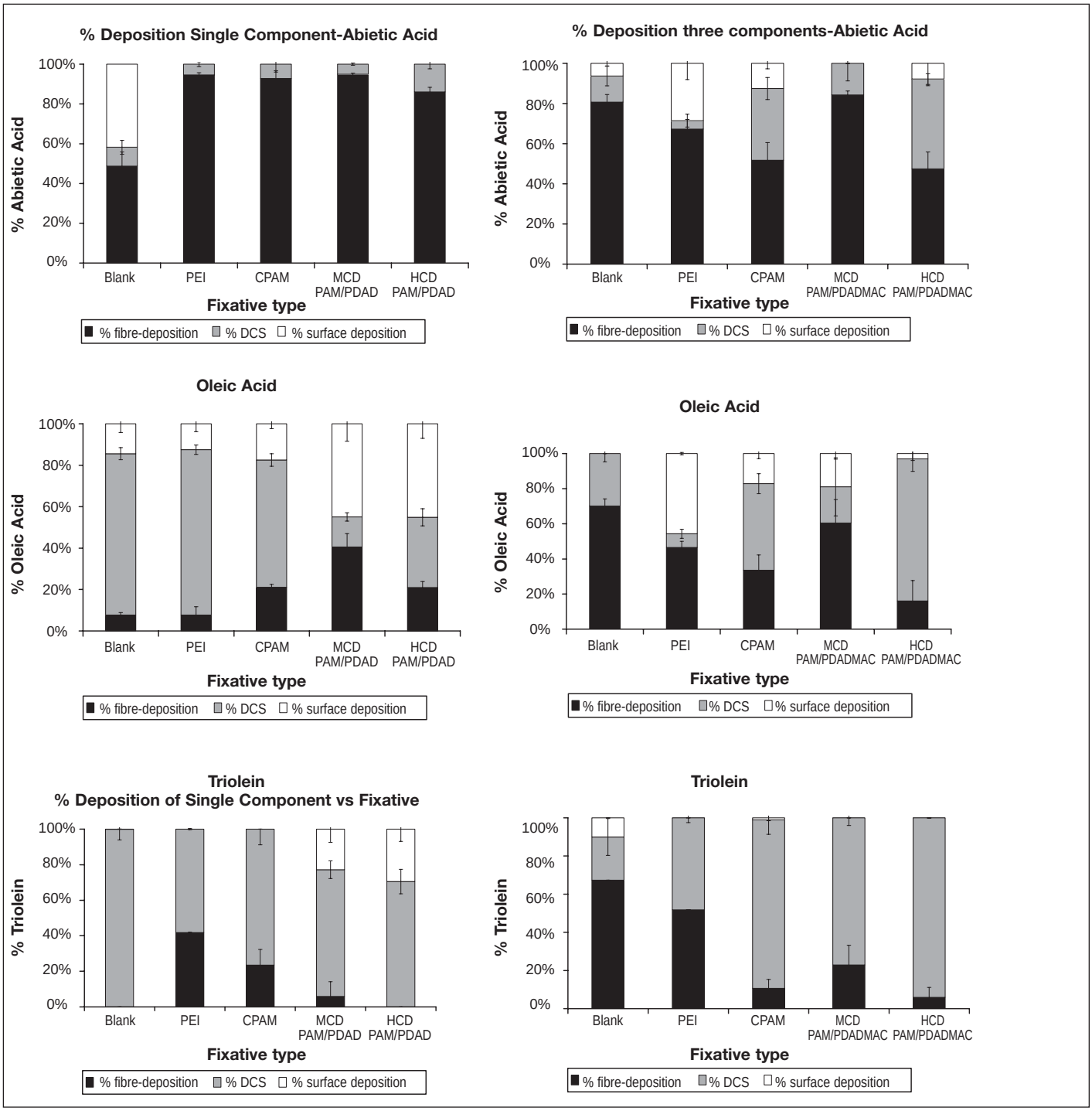

Fig. 4 Deposition of abietic acid, oleic acid and triolein in the presence of fibres (Error bars indicate ±1 std.dev. from mean)

dispersion that was prepared shows that 50% of the total wood resin is bound to the fibre and 40% is in the dissolved and colloidal phase. Each fixative was found to increase the total amount of pitch bound to the fibres. Some differences in the amount deposited onto non-fibre surfaces, and in the colloidal phase, were found. CPAM and two the co-polymers appear to be more effective at bonding the pitch to the fibres in preference to non-fibre surfaces as compared to PEI. The MCD co-polymer was found to produce the highest fixation of the wood resins onto fibres. The experiments in the absence of fibres indicated PEI was either not interacting with the extractives or interacting and causing surface deposition. These results support the latter assumption as PEI causes the most deposition on both fibres and other surfaces.

Some interesting results were found when the individual component concentrations present in the fibre bound, non-fibre bound and dissolved colloidal fractions were investigated as shown in Figure 4. The addition of the fibres appears to affect the deposition tendency of the extractives when present as a single component. In the absence of fibres and when no fixative is added (Fig. 1) all the wood extractives showed very high deposition tendency (90+% deposition) however the results in Figure 4 indicate that only resin acid shows any strong deposition tendency, adsorbing on both the fibre and the non-fibre surfaces. The oleic acid and the triolein were found to exist in the dissolved colloidal phase when fibres are present. This suggests that something in the fibres may be contributing to the stabilisation of these extractives. It is well

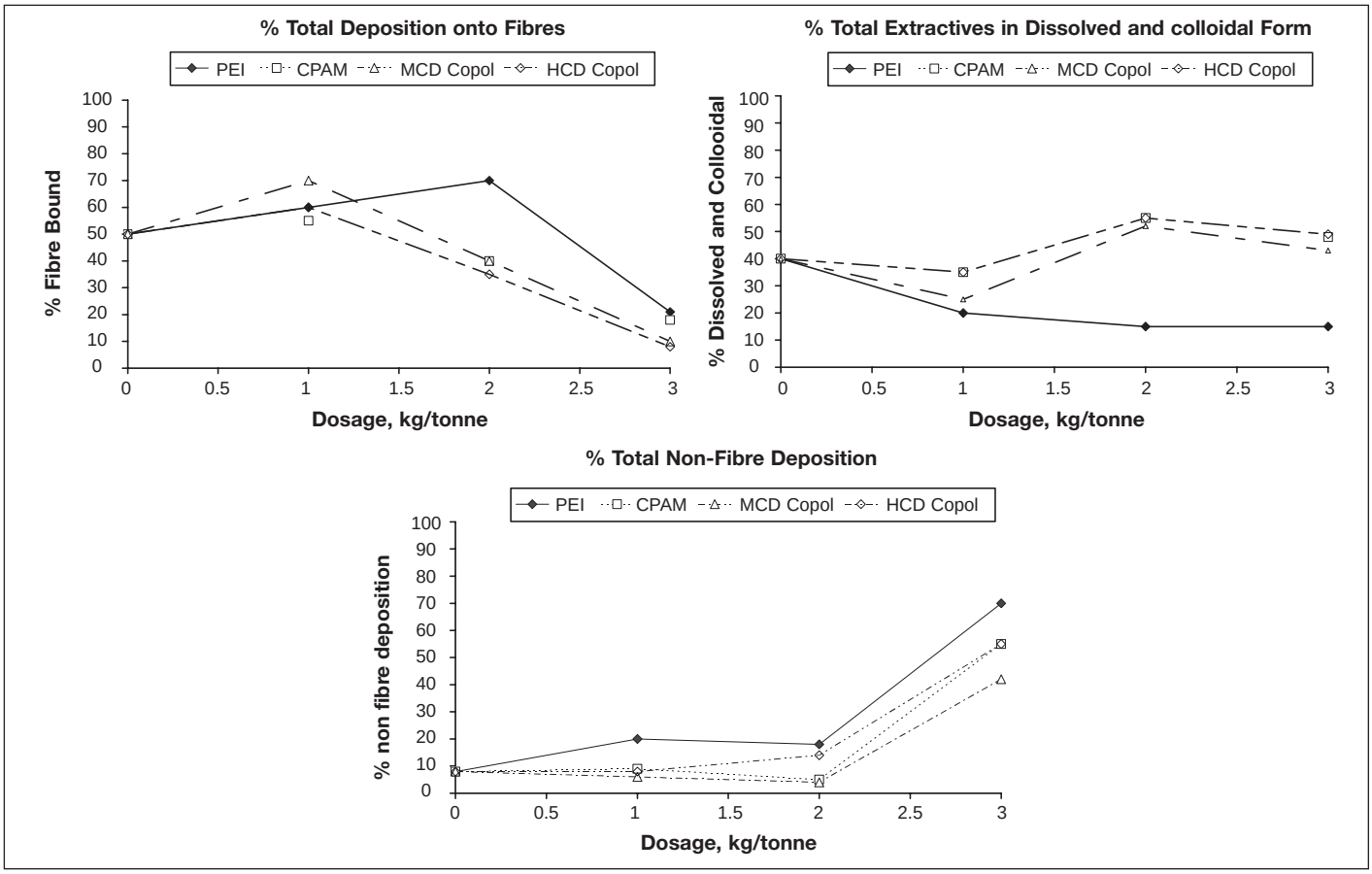

Fig. 5 Effect of polymer dose on amount of total extractives in a three component system

know that carbohydrates present in pulp suspensions stabilise pitch dispersions and so it is possible that some of this material present in the hexane extracted pulp is liberated when the pulp is redispersed in water and is able to stabilise all the oleic acid and triolein and some of the abietic acid but not all of it.

The fixatives (at 1kg/tonne addition) appear to show differences in their interaction with the individual extractives and also in their ability to fix the extractives to fibres and non-fibre surfaces. All the fixatives were found to increase the amount of abietic acid bound to the fibres, with little deposition onto other surfaces. Oleic acid, however, behaves quite differently. PEI seems to have little effect on the behaviour of the oleic acid. CPAM and the co-polymers cause an increase in the fibre-bound fraction and also the non-fibre surface bound fraction of oleic acid. PEI and CPAM bind more triolein to fibres, whilst the co-polymers cause the most surface deposition.

When the three pitch components are mixed together, significantly more oleic acid and triolein are deposited onto the fibre surface in the absence of fixatives compared to when they are present individually in a single component system. The findings indicate that some of the triolein is being deposited with the abietic and oleic acid as a result of an interaction. This is further support for the proposed colloidal model, where the triolein forms an inner hydrophobic core and is surrounded by the interacting hydrophilic groups such as fatty and resin acid groups, which form a hydrophilic outer shell (*1*). The results also indicate that whatever is stabilising the oleic acid and triolein when they present as a single component is not able to stabilise the three component complex. This may be due to the abietic acid forming the outer layer of the three component complex and the stabilising material does not stabilise abietic acid as well as oleic acid and triolein.

Unlike the single component system, the addition of the fixatives to the three component system with fibres appears to cause a decrease in the fibre bound fraction of the three extractives. PEI was found to increase the deposition of abietic acid and oleic acid onto non-fibre surfaces but appeared to have little effect on the triolein. CPAM and the two co-polymers appear to increase the amount of each extractive in the dissolved colloidal fraction indicating that they may be stabilising the three component complex in the aqueous phase.

The effect of polymer dose on the distribution of the pitch between the fibre bound, non-fibre and colloidal fractions is shown in Figure 5. The results indicate that adding more fixative does not result in more extractives being bound onto the fibres. It appears that at higher dosages (above 2kg/tonne) the selectivity of the fixatives in binding the extractives onto fibres declines and the extractives are fixed to non-fibre surfaces. Differences in the dissolved and colloidal fraction were evident. PEI, was found to reduce the amount of extractives in the dissolved colloidal phase while the other fixatives increased the amount of material in this fraction.

All the fixatives show similar behaviour in fixing all the pitch to the fibre fraction with each having a maximum in fibre bound deposition at 1-2 kg/tonne. However further investigation into the effects of the fixatives on the individual components showed differences (Fig. 6).

Addition of CPAM and the co-polymers result in only minor fixation of triolein across all dosage levels. The major difference is the ability of PEI to fix the

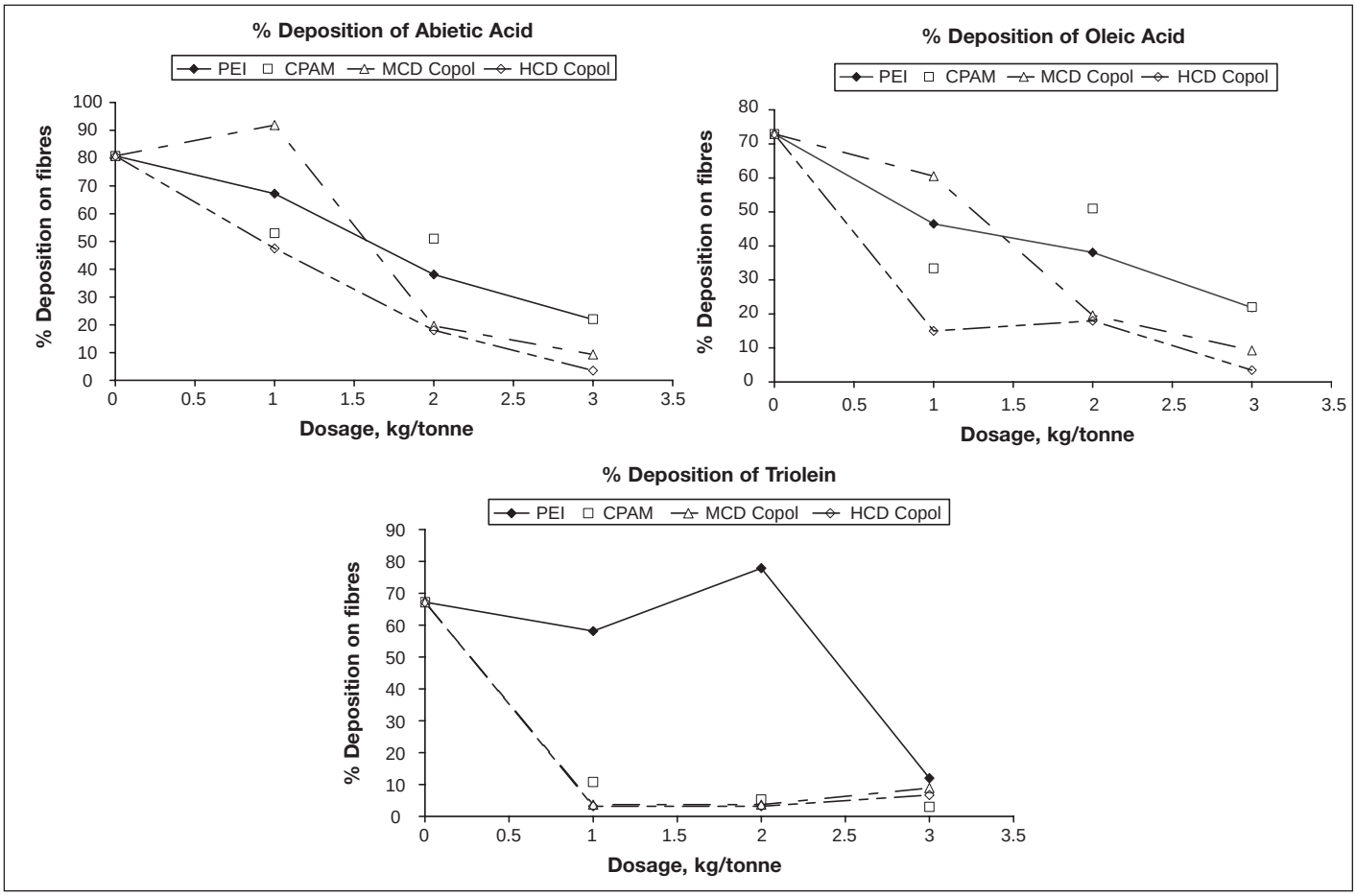

Fig. 6 Fixation of abietic acid, oleic acid and triolein onto fibres at different dosages

triolein onto fibres. Across all dosage levels the fixation performance is significantly higher than any other fixative. The ability of PEI to fix the triolein drops at 3kg/tonne dosage.

Adsorption of fixatives onto fibres

Further characterisation of the fixatives was performed in an attempt to understand the deposition results and to determine how much of each polymer was adsorbed by the fibres. The attraction of the cationic polymers to the negatively charged polymer surface was investigated by adding 1, 2 and 3kg/tonne doses of the fixative to a 1% stock consistency fibre suspension and stirring the mixture for 30 minutes (as was done in the deposition studies). The solution was then filtered and the supernatant titrated with PES-Na to determine the charge demand. Thus, the amount of cationic polymer unattached to the fibre surface and remaining in solution was being measured. The results are shown in Figure 7.

The medium charge density co-polymer was the least adsorbed onto the fibres and had the greatest amount of polymer in solution at all dosage levels. Similarly, CPAM was also found in solution at all polymer dosages (Fig. 7). Excess polymer in solution is expected to result in colloidal stabilisation of the wood extractives, as the polymer has a lower affinity to the fibres and the predominant reaction would be with the extractives. The results in Figure 8 show that CPAM along with the co-polymers seem to stabilise the abietic acid, oleic acid and triolein in solution across all dosages levels.

PEI and the highly charged co-polymer showed the greatest adsorption onto the fibre-surface. At the 1kg/tonne dosage, all of the PEI was adsorbed, with an excess in solution found at the 2 and 3kg/tonne dosages. This corresponds to the deposition studies as PEI was observed to cause either surface or fibre deposition, with minor stabilization in solution. The highly charged co-polymer was also expected to exhibit a preference for adsorption onto fibres (*16*). This was predicted as highly charged polymers strongly attach to the fibre-surface with fewer loops and tails. Whilst PEI exhibit-

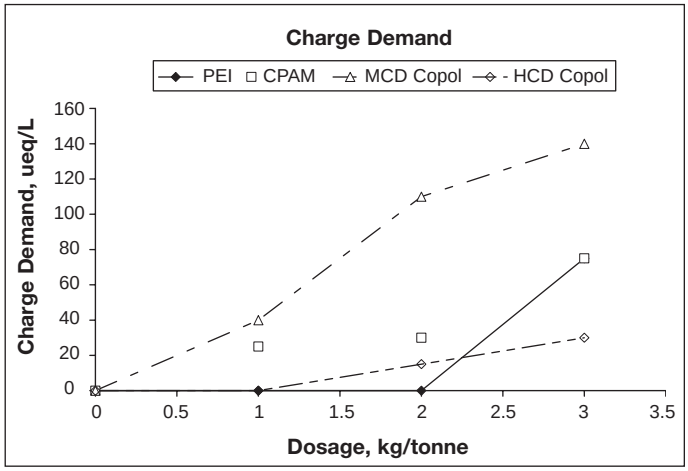

Fig. 7 Charge demand of the supernatant

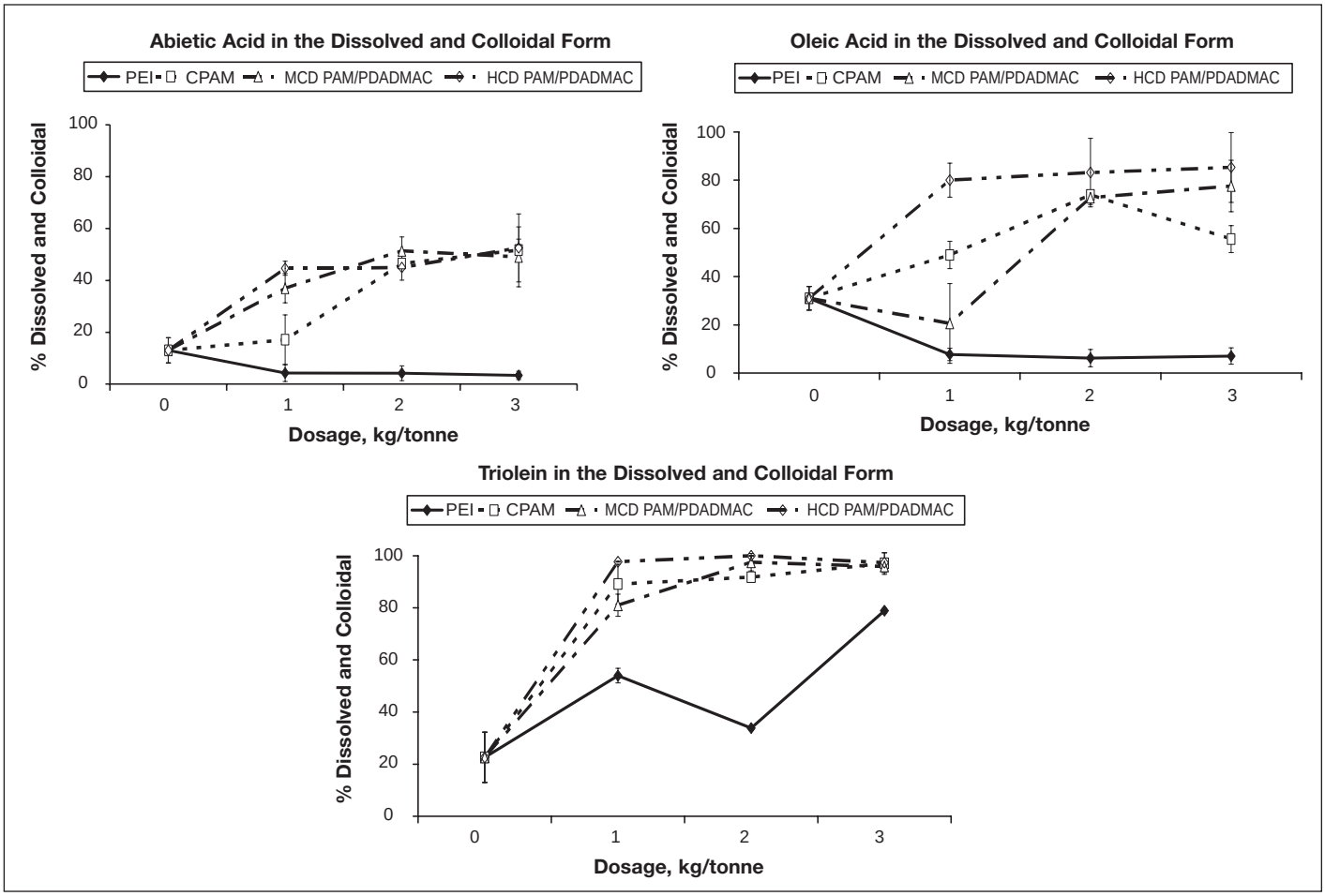

Fig. 8 Dissolved and colloidal fraction of abietic acid, oleic acid and triolein in the triple-component system in the presence of fibres (Error bars indicate ±1 std.dev. from mean)

Table 2
Summary of charge, stabilisation and fixation behaviour of polymers.

Charge Density	HCD> PEI> MCD> CPAM
Adsorption onto fibres	PEI> HCD>CPAM> MCD
Fixation of pitch onto fibres	
RA	MCD>PEI>CPAM>HCD
FA	MCD>CPAM>HCD>PEI
TG	PEI>CPAM>MCD>HCD
3 component complex	PEI≥MCD>CPAM>HCD
Stabilisation of pitch into DCS	HCD>CPAM>MCD>PEI

ed deposition to all surfaces, the highly charged co-polymer exhibited a preference for fibre-attachment or stabilization of the colloid in solution. This was thought to be a result of its chemical structure, as a similar preferential behaviour was observed for the medium charged co-polymer.

It is generally thought that fixatives function via the patch-charge or bridging mechanism such that the extractives ultimately become part of the final paper sheet. The results, however, do not conclusively show this. It appears that both fibre fixation and stabilisation of the three component pitch colloid occurs with the addition of CPAM and the two co-polymers. PEI appears to behave differently in that it fixes the pitch to the fibres and also causes fixation to other surfaces without stabilising the pitch in solution. It appears to be more effective at binding triolein as a single component and also as part of the three component complex.

There appears to be very little correlation between the charge density of the fixatives and their deposition behaviour as shown in Table 2. Although the HCD co-polymer had the highest charge density, PEI seemed to be more strongly adsorbed to the fibres, CPAM was found to stabilise the colloids to a similar extent as the HCD co-polymer and the MCD co-polymer appeared to fix abietic acid and oleic acid better than the other fixatives. Other factors appear to be contributing to the differences observed in both interaction with the fibres and deposition behaviour. Work is currently underway to investigate the effect of chemical structure on the interaction between fixatives and wood resins using computer molecular modelling techniques.

The differences in behaviour between the four fixatives suggests that a multi-component fixative system may be needed to optimise the fixation and stabilisation of the pitch components to minimise pitch deposition.

CONCLUSIONS

The behaviour of fixatives and model pitch compounds appears to be quite complex with many different interactions occurring. The deposition tendency of the colloidal pitch dispersions is greatly influenced by the interactions with each other and also the presences of fibres. Table 3 summarises the behaviour.

When added individually abietic acid, oleic acid and triolein all show strong

Table 3
Summary of Deposition Behaviour of wood resins

	No Fixative	PEI	CPAM	Co-polymer
Absence of fibres Single components	• RA, FA and TG all have very high deposition tendency	• Very little effect on RA and FA deposition tendency • Stabilises some of TG	• Stabilies allthree in solution	• Stabilises all three in in solution with HCD>MCD
Absence of fibres 3 components together	•Triolein stabilised by small amount of RA and FA • Remaining RA and FA was very high deposition tendency	• Increases the deposit-ability of 3 component complex	• Increases the deposit-ability of 3 component complex • Stabilises remaining RA and FA	• Stabilises the complex in solution along with the remaining complex
With Fibres Single components	• 50% RA bound to fibre and 40% to other surfaces • Most of FA and TG in DCS being stabilised by something in pulp	• Increases amount of RA and TG fixed to fibres	• Increases the amount of all three fixed to fibres	•Increases the amount of RA and FA bound to fibres • Increases the amount of FA and TG bound to other surfaces
With Fibres 3 components together	• Deposit-ability of each is greater when all 3 present possible due to interactions with RA	• Increases the amount of each bound to other surfaces	• Increases the amount of each in DCS	• Increases the amount in DCS with HCD>MCD

Key:
RA-resin acid (abietic acid)
FA- fatty acid (oleic acid)
TG- triglyceride (triolein)
DCS- dissolved/ colloidal substances

deposition tendency in the absence of fibres. When added together triolein appears to be stabilised by the interaction with abietic acid and oleic acid. The complex formed appears to contain all the triolein and only a small amount of fatty acid and resin acid. The excess abietic acid and oleic acid could either form a more loosely held layer around the wood extractive colloid or form a separate two component complex that is more hydrophobic than the three component complex. Further work is needed to clarify this.

The fixatives were found to reduce the stability of the three component pitch complex but increase the stability of the other colloidal species present containing abietic and oleic acid, in the absence of fibres.

When fibres are present stabilisation of oleic acid and triolein occurs. This is possibly due to the release of stabilising carbohydrate material present in the extracted pulp. When the three components are together with fibres greater fixation of triolein and oleic acid occurs because of the interaction between the three components.

All four of the fixatives were found to bind the majority of abietic acid onto the fibres, when it was present by itself. The medium charged co-polymer was found to attach more abietic acid and oleic acid to fibres, when they are present together, whilst PEI attached the most triolein.

The fixatives appear to do more than fix the pitch components to the fibres. CPAM and the PAM/polyDADMAC co-polymers were also found to stabilise the pitch complexes in the dissolved and colloidal fraction. PEI, on the other hand, was found to be strongly adsorbed onto the fibre and caused both fixative to the fibres and non-fibre surfaces. PEI did not stabilise the pitch in the dissolved and colloidal fraction, as did the other polymers.

Increasing addition rate of the fixative does not always result in more fixation of pitch to fibres but in fact the reverse with more fixation of pitch onto non-fibre surfaces (i.e. overdosing is possible).

A combination of two or more fixatives that act in different ways may be needed to optimise the fixation and stabilisation of colloidal pitch in order to prevent pitch deposition.

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